Application Of Pyroelectric Crystal And Ionic Liquid To The Production Of Metal Compounds

AUTHOR(S):

Imashuku, Susumu; Imanishi, Akira; Kawai, Jun

CITATION:

Imashuku, Susumu ...[et al]. Application Of Pyroelectric Crystal And Ionic Liquid To The Production Of Metal Compounds. AIP Conference Proceedings: Application of Accelerators in Research and Industry 2013, 1525: 305-308

ISSUE DATE:

2013-04-19

URL:

http://hdl.handle.net/2433/187971

Application Of Pyroelectric Crystal And Ionic Liquid To The Production Of Metal Compounds

Susumu Imashuku, Akira Imanishi, and Jun Kawai

Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

Abstract. Zinc fluoride (ZnF_2) was deposited on a silicon substrate by changing temperature of a pyroelectric crystal of $LiTaO_3$ on which ionic liquid (EMI-Tf_2N) containing zinc ions was dripped at 1 Pa. ZnF_2 was also obtained by bombarding argon ions on EMI-Tf_2N containing zinc ions. From these results, it is concluded that EMI-Tf_2N containing zinc ions on the $LiTaO_3$ crystal was evaporated on the silicon substrate by changing temperature of the $LiTaO_3$ crystal in vacuum and that the evaporated EMI-Tf_2N containing metal zinc ions was decomposed to ZnF_2 by the bombardment of electrons accelerated by the electric field between the $LiTaO_3$ crystal and the silicon substrate.

Keywords: Pyroelectric crystal, Ionic liquid, Metal fluoride, XPS
PACS: 82

INTRODUCTION

When a temperature change under a vacuum condition around 1 Pa is applied to a pyroelectric crystal such as lithium tantalate ($LiTaO_3$) and lithium niobate ($LiNbO_3$), an electric field is produced due to uncompensated charge on the surface of the pyroelectric crystal. For example, 50 kV can be obtained by applying a temperature difference of 80 K to a pyroelectric crystal of $LiTaO_3$ with 3 mm × 3 mm in x-y plane and 5 mm in z-axis at 1 Pa. Then, small amounts of suspended electrons and ions in the condition are accelerated by the produced electric field. Brownridge first generated X-rays using a pyroelectric crystal of $CsNO_3$ and gold foil as a target.[1] After that, several researchers have been working on the application of pyroelectric crystals to X-ray generator with high enery,[2-5] electron and ion beams,[6] ion source for mass spectrometry,[7] and an electron source for electron probe X-ray microanalyzer.[8] In the present study, we applied the high voltage produced with the pyroelectric crystal to a production of metal compounds such as fluoride and sulfide. We selected an ionic liquid containing metal ions as a reactant because ionic liquid has low vapor pressure. The produced electric field is expected to be effectively applied to the ionic liquid because ionic liquid has high ionic conductivity.

EXPERIMENTAL

Figure 1 shows a schematic view of the experimental set-up in the present study. +z plane of a single crystal of $LiTaO_3$ with 3 mm × 3 mm in x-y plane and 5 mm in z-axis was attached on a Peltier device with silver paste. Ionic liquid, EMI-Tf_2N (1-Ethyl-3-methylimidazolium bis (trifluomethylsulfonyl) imide) whose structure was shown in Fig. 2, containing 1 mol L^{-1} zinc ion (Zn^{2+}) was dripped on the $LiTaO_3$ crystal. EMI-Tf_2N containing zinc ions was produced by dissolving $Zn(Tf_2N)_2$ into EMI-Tf_2N. $Zn(Tf_2N)_2$ was prepared according to the reported literature.[9] The other face of the Peltier device was attached on a copper rod with silver paste. The copper rod with a hole in the center was connected to a rotary vane pump. The temperature of the $LiTaO_3$ crystal was controlled by connecting the Peltier device to DC power supply. A silicon substrate was attached on anther copper rod with silver paste. The distance between the pyroelectric crystal and substrate was set to 30 mm. The chamber was sealed with detachable vacuum joints (quick release couplings). The two copper rods were grounded in order to keep the electric potential of the substrate the same as +z plane of the $LiTaO_3$ crystal. The $LiTaO_3$ crystal was heated at 100 °C for 2 minutes by applying +3 volt DC to the Peltier device. Then, the $LiTaO_3$ crystal was cooled at 5 °C for 2 minutes by applying −3 volt DC to the Peltier device. This heating and cooling cycle was

Application of Accelerators in Research and Industry
AIP Conf. Proc. 1525, 305-308 (2013); doi: 10.1063/1.4802338

repeated twenty times. Pressure of the chamber was set to 2 Pa. During the heating and cooling cycle of the $LiTaO_3$ crystal, about 50 kV was applied between the $LiTaO_3$ crystal and the substrate.[8] The precipitates of the substrates were investigated by X-ray photoelectron spectroscopy (JPS-9010TRX, JEOL) with a non-monochromated Mg Kα X-ray source. The energy resolution was 1.3 eV measured as a full-width at half maximum (FWHM) of the Ag $3d_{5/2}$ line. The pressure during the measurements was kept below 3 × 10^{-6} Pa. The obtained spectra were corrected using the Ag $3d_{5/2}$ or Si 2p peak.

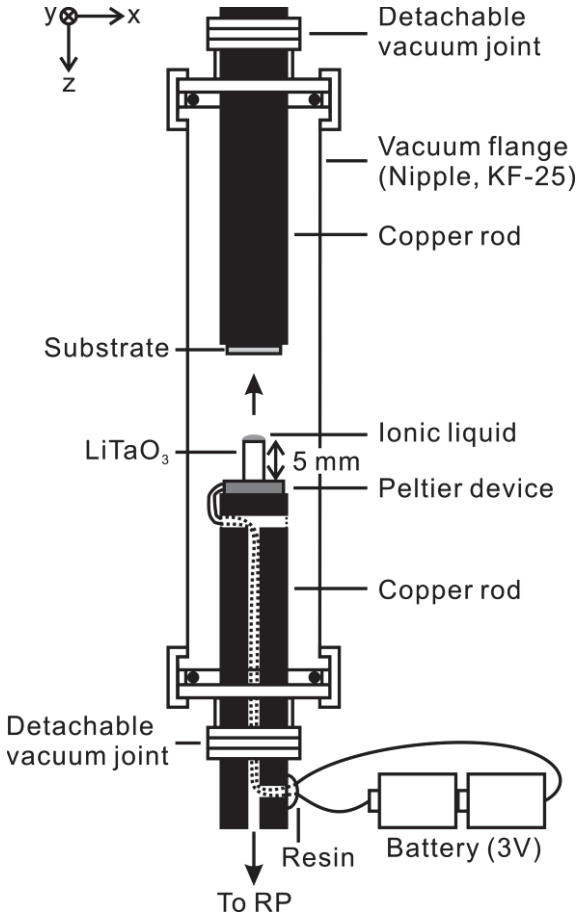

FIGURE 1. Schematic view of the set-up.

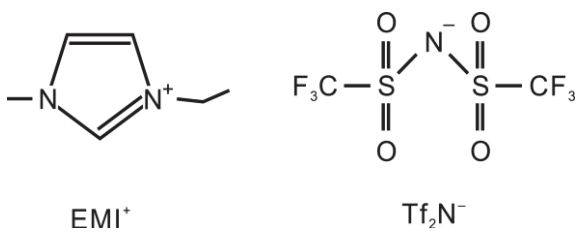

FIGURE 2. Structures of EMI-Tf_2N.

RESULTS AND DISCUSSION

Figure 3 show XPS spectra around Zn 2p, F 1s, O 1s, N 1s, C 1s, and S 2p of the silicon substrate after changing temperature of the $LiTaO_3$ crystal on which EMI-Tf_2N containing metal zinc ions was dripped with an XPS spectrum of EMI-Tf_2N containing zinc ions. Zn $2p_{1/2}$ and $2p_{3/2}$ peaks were detected on the silicon substrate. Although the intensity ratio of C 1s peaks at 285.5 and 286.9 eV changed, F 1s (688.7 eV), O 1s (532.5eV), N 1s (399.9 and 402.4eV), C 1s (285.5, 286.9, and 293.4 eV), and S 2p (169.4 eV) peaks related to EMI-Tf_2N were detected on the silicon substrate after changing temperature of the $LiTaO_3$ crystal on which EMI-Tf_2N containing metal zinc ions was dripped. The position of N 1s, C 1s, and S 2p peaks related to EMI-Tf_2N were coincident with reported values.[10-13] This result indicates that ions such as Zn^{2+}, EMI^+, and Tf_2N^- were field-emitted from EMI-Tf_2N containing zinc ions or that EMI-Tf_2N containing zinc ions was evaporated on the silicon substrate. F 1s peak of 684.7 eV was additionally detected on the silicon substrate after applying electric field to EMI-Tf_2N containing zinc ions as shown in Fig. 3 (b). The additional F 1s peak of 684.7 eV was closed to F 1s peak of zinc fluoride (ZnF_2). Other additional peaks were not detected after changing temperature of the $LiTaO_3$ crystal on which EMI-Tf_2N containing metal zinc ions was dripped. When argon ions accelerated with the voltage of 300 V were bombarded on EMI-Tf_2N containing zinc ions, F 1s peak was also detected at 685.1 eV which was closed to F 1s peak of ZnF_2, but F 1s peak related to Tf_2N^- was not detected as shown in Fig. 4. On the other hand, when argon ions were bombarded on EMI-Tf_2N without zinc ions, the F 1s peak related to Tf_2N^- was detected, but F 1s peak closed to ZnF_2 peak was not detected. These results suggest that EMI-Tf_2N containing zinc ions was decomposed to ZnF_2 by bombarding argon ions on EMI-Tf_2N containing zinc ions. In addition, vapor pressure of EMI-Tf_2N is calculated to be 1.2 × 10^{-5} Pa at 100 °C in contrast to 2.8 × 10^{-10} Pa at 25 °C.[14-16] Therefore, by changing temperature of the $LiTaO_3$ crystal on which EMI-Tf_2N containing zinc ions was dripped, EMI-Tf_2N containing zinc ions on the $LiTaO_3$ crystal was evaporated on the silicon substrate and then the evaporated EMI-Tf_2N containing zinc ions was decomposed to ZnF_2 by the bombardment of suspended electrons accelerated by the electric field between the $LiTaO_3$ crystal and the silicon substrate. However, reproducibility of the detection of the F 1s peak related to ZnF_2 was not confirmed using the $LiTaO_3$ crystal. This poor reproducibility is related to the thickness of ionic liquid on both the $LiTaO_3$ crystal

and substrate. A static dielectric constant of EMI-Tf_2N (ε_r = 15.2)[17] was lower than that of $LiTaO_3$ (ε_r ~ 40).[18-22] Thus, energies of electrons bombarded on the substrate decrease with increasing the thickness of EMI-Tf_2N containing zinc ions on the $LiTaO_3$ crystal and/or substrate because electric field between the $LiTaO_3$ crystal and substrate decrease. Therefore, EMI-Tf_2N containing zinc ions is not decomposed to ZnF_2 if the amount of EMI-Tf_2N containing zinc ions on $LiTaO_3$ crystal and/or substrate is large.

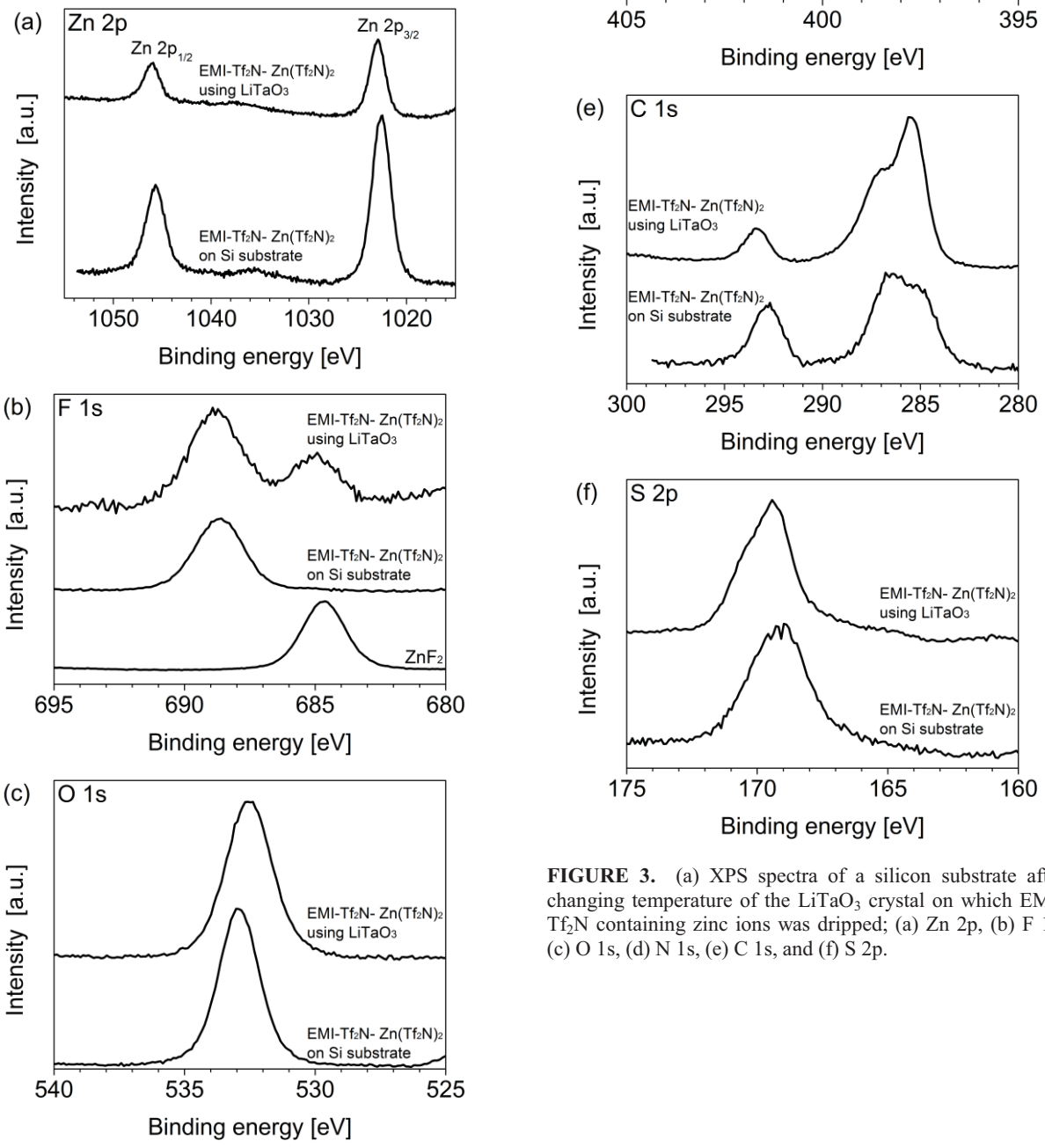

FIGURE 3. (a) XPS spectra of a silicon substrate after changing temperature of the $LiTaO_3$ crystal on which EMI-Tf_2N containing zinc ions was dripped; (a) Zn 2p, (b) F 1s, (c) O 1s, (d) N 1s, (e) C 1s, and (f) S 2p.

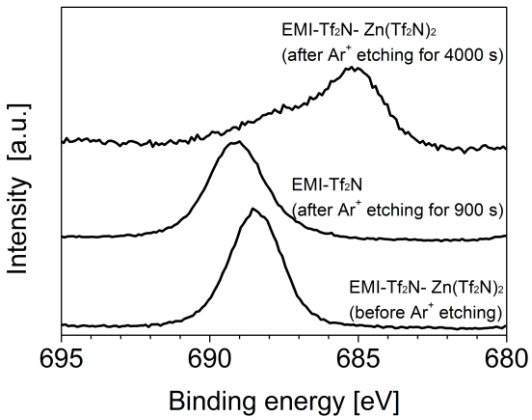

FIGURE 4. XPS F 1s spectra of EMI-Tf_2N containing zinc ions and EMI-Tf_2N after bombarding argon ions accelerated with the voltage of 300 V with an XPS spectrum of EMI-Tf_2N containing zinc ions before bombarding argon ions.

CONCLUSIONS

We obtained thin ZnF_2 film by changing temperature of a pyroelectric crystal of $LiTaO_3$ on which an ionic liquid (EMI-Tf_2N) containing zinc ions was dripped at 1 Pa. EMI-Tf_2N containing zinc ions was evaporated on a silicon substrate and then the evaporated EMI-Tf_2N containing zinc ions was decomposed to ZnF_2 by the bombardment of electrons accelerated by the electric field between the $LiTaO_3$ crystal and the substrate. The thickness of EMI-Tf_2N containing zinc ions layer on $LiTaO_3$ crystal and substrate is an important factor for forming the ZnF_2 film. When the amount of EMI-Tf_2N containing zinc ions on $LiTaO_3$ crystal and substrate is large, ZnF_2 film is not formed. Electrons bombarded on the substrate do not have enough energy to decompose EMI-Tf_2N containing zinc ions to ZnF_2 because a static dielectric constant of EMI-Tf_2N is lower than that of $LiTaO_3$ crystal.

ACKNOWLEDGMENTS

The present study was financially supported by the Kyoto Technoscience Center. We express our deep acknowledgement to Mr. Y. Sonobayashi for XPS measurements.

REFERENCES

1. J.D. Brownridge, *Nature* **358**, 287-288 (1992).
2. J.D. Brownridge and S.J. Reboy, *J. Appl. Phys.* **86**, 640-649 (1999).
3. J.A. Geuther and Y. Danon, *J. Appl. Phys.* **97**, 104916 (2005).
4. E. Hiro, T. Yamamoto, and J. Kawai, *Adv. X-ray. Chem. Anal., Japan* **41**, 195-200 (2010).
5. S. Imashuku and J. Kawai, *Rev. Sci. Instrum.* **83**, 016106 (2012).
6. J.D. Brownridge and S.M. Shafroth, *J. Appl. Phys.* **79**, 3364-3366 (2001).
7. E.L. Neidholdt and J.L. Beauchamp, *Anal. Chem.* **79**, 3945-3948 (2007).
8. S. Imashuku, A. Imanishi, and J. Kawai, *Anal. Chem.* **83**, 8363-8365 (2011).
9. T. Katase, T. Onishi, S. Imashuku, K. Murase, T. Hirato, and Y. Awakura, *Electrochemistry* **73**, 686-691 (2005).
10. S. Caporali, U. Bardi, and A. Lavacchi, *J. Electron Spectrosc. Relat. Phenom.* **151**, 4-8 (2006) 4.
11. O. Höfft, S. Bahr, M. Himmerlich, S. Krischok, J.A. Schaefer, V. Kempter, *Langmuir* **22**, 7120-7123 (2006).
12. S. Krischok, M. Eremtchenko, M. Himmerlich, P. Lorenz, J. Uhlig, A. Neumann, R. Öttking, W.J.D. Beenken, O. Höfft, S. Bahr, V. Kempter, J.A. Schaefer, *J. Phys. Chem. B* **111**, 4801-4806 (2007).
13. T. Kurisaki, D. Tanaka, Y. Inoue, H. Wakita, B. Minofar, S. Fukuda, S. Ishiguro, Y. Umebayashi, *J. Phys. Chem. B* **116**, 10870-10875 (2012).
14. D.H. Zaitsau, G.J. Kobo, A.A. Strechan, Y.U. Paulechka, A. Tschersich, S.P. Verevkin, A. Heintz, *J. Phys. Chem. A* **110**, 7303-7306 (2006).
15. J.M.S.S. Esperanca, J.N.C. Lopes, M. Tariq, L.M.N.B.F. Santos, J.W. Magee, L.P.N. Rebelo, *J. Chem. Eng. Data* **55**, 3-12 (2010).
16. D.H. Zaitsau, S.P. Verevkin, V.N. Emel'yanenko, A. Heintz, *Chem. Phys. Chem.* **12**, 3609-3613 (2011).
17. C. Wakai, A. Oleinikova, M. Ott, H. Weingärtner, *J. Phys. Chem. B* **109**, 17028-17030 (2005).
18. A. W. Warner, M. Onoe, and G. A. Coquin, *J. Acoust. Soc. Amer.* **42**, 1223-1231 (1967).
19. R.T. Simith and F.S. Welsh, *J. Appl. Phys.* **42**, 2219-2230 (1971).
20. T. Yamada, N. Niizaki, and H. Toyoda, J*pn. J. Appl. Phys.* **6**, 151-155 (1967).
21. G. Kovacs, M. Anhorn, H. E. Engan, G. Visintini, C.C.W. Ruppel, "Improved Material Constants for $LiNbO_3$ and $LiTaO_3$" in *IEEE 1990 Ultrasonics Symposium*, edited by B.R. Mcavoy, IEEE 1990 Ultrasonics Symposium 1990 Proceedings 1, The Institute of Electrical and Electronics Engineers Inc., 1990, pp. 435-438.
22. J. Kushibiki, I. Takanaga, M. Arakawa, T. Sannomiya, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **46**, 1315-1323 (1999).